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(54) Title of Invention: **FLEXOGRAPHIC PRINTING PLATE WITH IMPROVED PRINTING QUALITY**

(57) Abstract

[Problem]

To provide a photosensitive resin-based flexographic printing plate with excellent ink transferability in the solid [image] areas.

[Means Used to Solve the Problem]

A flexographic printing plate is used which has a plate surface average roughness of 0.1 to 0.6μm.

[Claims]

[Claim 1]

A flexographic printing plate having a plate surface average roughness of 0.1-0.6μm.

[Claim 2]

A flexographic printing plate as set forth in Claim 1, wherein the plate has a surface tension of 35dyne/cm or greater.

[Claim 3]

A process for the manufacture of the flexographic printing plate as set forth in Claim 1, which processes comprises

laminating a slip layer (b) having a rough surface with an average surface roughness of 0.1 to 0.6μ, onto a photosensitive resin layer (a),

said resin layer comprising

50% by weight or more of a thermoplastic elastomer composed of at least one monovinyl substituted aromatic hydrocarbon and conjugated diene, 1-20% by weight of at least one ethylenic unsaturated compound, and 0.1 to 3% by weight of at least one photopolymerization initiator,

in such a way that the rough surface thereof comes in contact with the layer (a).

[Claim 4]

A process for the manufacture of a flexographic printing plate as set forth in Claim 3, wherein the slip layer (b) is comprised of at least one polyamide and at least one thermoplastic elastomer, said thermoplastic elastomer being present in an amount of 0.1-30% by weight of the total [weight] of the slip layer (b).

[Claim 5]

A process for the manufacture of a flexographic printing plate as set forth in Claim 4, wherein the thermoplastic elastomer contained in the slip layer (b) is a thermoplastic elastomer comprising at least one monovinyl substituted aromatic

hydrocarbon and conjugated diene, or a thermoplastic elastomer comprised of hydrogenated blocks of a monovinyl substituted aromatic hydrocarbon and conjugated diene.

[Claim 6]

A process for the manufacture of a flexographic printing plate as set forth in Claims 4 and 5, wherein the slip layer (b) is derived from a composition comprised of at least one polyamide and at least one thermoplastic elastomer.

[Claim 7]

A process for the manufacture of a flexographic printing plate as set forth in Claims 3-6, which process comprises

dissolving slip layer components in a solvent, coating the solution on a polyester film, and drying off the solvent thereby generating the slip layer (b) on said film; and

laminating said slip layer (b) onto the photosensitive resin layer (a) in such a way to permit the surface of the slip layer not facing the polyester film to come in contact with the photosensitive resin layer (a).

[Claim 8]

A flexographic printing plate as set forth in Claim 1 and 2 wherein it is prepared by any one of the processes set forth in Claims 3-7.

[Detailed Explanation of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to a flexographic printing plate having excellent printing quality.

[0002]

[Prior Art]

Among those flexographic printing plates extensively used heretofore are rubber cast plates and photosensitive resin plates prepared by plate-making from photosensitive resin compositions. However, recent advances in flexographic printers and ink enable the achievement of high printing quality and have made it possible to begin replacing the traditional offset and gravure systems by a flexographic printing system. For the printing plates used in high printing quality flexographic printing, the proportion of flexographic printing plates prepared by plate-making from a photosensitive resin composition has been on the rise because a fine image can be reproduced. It is a general practice for preparation of such photosensitive resin-based flexographic printing plates to use a photosensitive resin composition comprised of a polyester film support, at least one thermoplastic elastomer, an ethylenic unsaturated compound, and a radiation-reactive initiator.

[0003]

High printing quality desired in flexographic printing calls for having smallest dots as a printing image relief thereby excellently expressing highlight areas in a printing material and for transferring sufficient ink to the plate for solid areas thereof. It is, however, not easy to simultaneously accomplish these two objectives, leaving many problems to overcome.

That is, in order to transfer a sufficient amount of ink to the substrate to be printed, applying a higher print pressure is effective, but that very pressure would subject even the smallest dots of the printing plate relief to an excessive pressure, thereby eventually collapsing these highlight's smallest dots and thusly failing to express the desired highlight areas. On the other hand, attempts to achieve a desired expression for the highlight areas by reducing the print pressure will be met with the inability to transfer a sufficient amount of ink to the substrate to be printed, a drop in so-called ink transferability, thereby causing the problem of printing irregularities in the print portions for solid areas of the printing plate.

[0004]

There have been disclosed photosensitive resin-based flexographic printing materials capable of forming extremely fine half-tone dots, such as a process taught in Unexamined Japanese Patent Application Publication, Kokai 2000-155418, but it says nothing about the printing plate prepared by this method regarding the ink transferability for the solid areas.

[0005]

[Problem to be Solved by the Invention]

The present invention addresses the problem of providing a photosensitive resin-based flexographic printing plate having excellent ink transferability in solid areas.

[0006]

[Means Used to Solve the Problem]

As a result of their extensive study of the problem mentioned above, the present inventors discovered that defining the surface average roughness of the printing plate as 0.1 to 0.6μm improves the ink transferability for the solid areas of a flexographic printing plate, in particular, by controlling, to a specific range, the average roughness of a slip layer that has heretofore been set up on the photosensitive resin layer of the photosensitive resin-based flexographic printing plate for smoothening the contact of a negative film therewith can effectively accomplish the above problems, which has led to the present invention.

[0007]

[Embodiment of the Invention]

The present invention is now specifically explained below. For the flexographic printing plates used in this invention, one may use a flexographic printing plate prepared by engraving natural rubber, or a flexographic printing plate obtained by plate making from a photosensitive resin. For the natural rubber, optionally one may use a grade which has been treated such as by vulcanization.

[0008]

The flexographic printing plate of this invention requires its plate surface average roughness to be 0.1-0.6μm. When the printing plate has an average surface roughness falling within this range, it exhibits good ink transferability, providing good printing quality in the solid areas of the substrate to be printed. The preferred range is 0.1-0.3μm, preferably 0.1-0.2μm. The roughness of the plate surface can be found by determining R_a, which is a center line average roughness defined by JIS Surface Roughness (B0601) (hereafter the center line average roughness is optionally referred to as "R_a"). R_a can be determined by a commercial measurement device. The center line average roughness can be determined by bringing the probe stylus into contact with the plate surface and scanning the plate surface. In addition, there is a device on the market that determines surface roughness from the reflection of laser light.

[0009]

It is preferred for the printing plate of this invention to have a surface tension of 35dyne/cm or greater. Having surface tension greater than that range will provide the printing plate surface with sufficient wettability to more readily hold a sufficient amount of ink on the plate surface so as to be able to transfer the necessary amount of ink to the substrate to be printed, a convenience in improving the ink transferability. Preferably, the tension should be 38dyne/cm or greater, more particularly, 40 dyne/cm or greater.

[0010]

The surface tension of the printing plate, which can be obtained by determining the contact angle between a droplet of a liquid with a known surface tension and the surface of a given printing plate, may be obtained by measuring contact angles with liquids having different surface tensions. The liquids with known surface tensions include water, ethanol, and the like. In addition, the methods for measuring the surface tension of printing plates include use of a wettability indicator. Such indicators can be prepared which have surface tensions in the range of 30-56dyne/cm by mixing ethylene glycol monoethylether and formamide at adjusted proportions. Applying such an indicator to the surface of a printing plate and observing the way the liquid film of the wettability indicator breaks

allows the determination of a surface tension of the plate.

[0011]

The surface tension of a printing plate prepared from a photosensitive resin can be adjusted by adjusting, at a suitable rate, the block ratio of the thermoplastic elastomer that constitutes the printing plate. Examples may be mentioned which include use of a block copolymer of polyisoprene and polystyrene or of polybutadiene and polystyrene, where the controlling the [block] ratio of the polyisoprene or polybutadiene with respect to the polystyrene allows adjusting the surface tension of the plate.

[0012]

The roughness of the printing plate surface of this invention can be adjusted by using a matted film and thereby transferring its roughness to the printing plate. For such films, one may use chemically treated or sandblasted polypropylene or polyester films. Another approach is to subject a photosensitive resin-based printing plate composition containing a support layer, photosensitive layer (a) and slip layer (b) to a plate-making process, thereby generating a flexographic printing plate having an adjusted plate surface average roughness.

[0013]

For the support layer, a dimensionally stable polyester film may be used which has a thickness ranging from 75 to 300µm. Optionally, a chemical or physical treatment may be carried out by performing a corona treatment, alkaline treatment, or sandblasting. The support may optionally be coated with an adhesive, for example, by a method disclosed in Unexamined Japanese Patent Application Publication Kokai 2000-155410. The photosensitive resin layer (a) can be molded into the desired configuration from a photosensitive resin composition. Generally used in the photosensitive resin compositions are those at least comprised of a thermoplastic elastomer, ethylenic unsaturated monomer, and photopolymerization initiator.

[0014]

For the thermoplastic elastomer, use is generally made of one prepared by polymerization of a monovinyl substituted aromatic hydrocarbon and a conjugated diene monomer. The monovinyl substituted aromatic hydrocarbon monomers used herein include styrene, α-methylstyrene, p-methylstyrene, p-methoxystyrene, and the like; the conjugate diene monomers include butadiene, isoprene, and the like. Typical examples include styrene-butadiene block copolymers and the like.

[0015]

For the ethylenic unsaturated monomers, one can use monomers that are conventionally used in photosensitive compositions such as acrylate esters of t-butyl alcohol, lauryl alcohol, or like alcohol; maleimide derivatives such as

lauryl maleimide, cyclohexyl maleimide, benzylmaleimide and the like, or fumarate esters with alcohols, such as dioctyl furalate, and the like, or esters of acrylic acid or methacrylic acid with polyhydric alcohols, such as hexanediol (meth) acrylate, nonanediol (meth) acrylate, trimethylol (meth) acrylate and the like, singly or in combination thereof for use in the photosensitive resin compositions.

[0016]

Known radical polymerization initiators may be used such as aromatic ketones, benzoyl ethers, and the like as photopolymerization initiators. It is possible to select for use from among benzophenone, Michler's ketone, benzoin methylether, benzoin ethylether, benzoin isopropylether, α-methylolbenzoin methylether, α-methoxybenzoin methylether, 2,2-diethoxy diphenylacetophenone, and the like, a combination thereof may also be used.

[0017]

Optionally, the photosensitive resin may further contain a sensitizer, thermal polymerization inhibitor, plasticizer, colorant, and the like. The above photosensitive resin composition may be used to prepare the photosensitive resin layer (a) of this invention by a variety of methods. For example, a composition such as the above can be prepared by dissolving the starting materials to be formulated in a suitable solvent such as chloroform, toluene, and the like and mixing, casting into a frame, and evaporating off the solvent. In addition, these ingredients may be milled with a kneader or rolls and made into a desired thickness using an extruder, injection molder, press, and the like.

[0018]

It is preferred for the slip layer (b) to use a composition comprised of a flexible polyamide and 0.1-30% by weight of at least one thermoplastic elastomer. An amount less than 0.1% by weight will not provide a sufficient close contact between the slip layer (b) and the resin, while an addition beyond that range will cause the surface of the slip layer (b) to be tacky, in the case of some types of the polyamide and thermoplastic elastomer used.

[0019]

Such flexible polyamides are on the market for use in hot-melt type adhesives, from which those effective for this invention can be selected, for example, the Macromelt series manufactured by Henkel Japan KK. Elastomers from monovinyl substituted aromatic hydrocarbons and conjugated dienes can be used as thermoplastic elastomer components in this invention. Examples include Tufprene series manufactured by Asahi Kasei KK or Kraton series made by Shell Chemicals, and the like.

[0020]

In order to suppress excess tack of the slip layer (b) when a thermoplastic elastomer is used, a thermoplastic elastomer comprised of monovinyl aromatic hydrocarbon and hydrogenated conjugated diene blocks may optionally be used, for which, for example, the Tuftec Series made by Asahi Kasei KK may be mentioned. For reducing the center line average roughness of the slip layer, it is preferred for the main component of the slip layer (b) to be a composition prepared by premixing the polyamide and thermoplastic elastomer. The polyamide and thermoplastic elastomer may be mixed by a method generally known in art, for example, using a single screw extruder, twin screw extruder, kneader, etc.

[0021]

The slip layer (b) of this invention may be generated from a resin composition prepared by dissolving the above individual resin components in a suitable solvent. In order to provide the flexographic printing plate with the desired surface average roughness, it is preferred for the slip layer prepared from the above resin composition (b) to have a center line average roughness in the range of 0.1-0.6μm. The slip layer (b) is prepared by uniformly coating a film having a suitably adjusted surface average roughness achieved by preliminarily sandblasting, chemical treating, or treating likewise a film such as polyethylene terephthalate or polypropylene, with a resin composition that generates the desired coated level of the slip layer (b) using a bar coater or gravure coater, or the like, followed by drying, thereby generating the slip layer (b). The amount coated after drying is normally 1-10g/m^2. Since the slip layer (b) receives an effect transferred from the film's surface average roughness, as prepared, it will have the desired surface average roughness on a side opposite to the side in contact with the film; and that side is laminated so as to be in contact with the above-mentioned photosensitive resin layer (a), thereby generating a printing plate structure, which in turn will result in a printing plate of this invention having the desired plate surface average roughness.

[0022]

For this printing plate structure it is preferred for the slip layer (b) to be soluble in the developer solution. A slip layer (b) insoluble in the developer solution, requiring an extra step for removal of the protective film, is undesirable from the standpoint of plate-making efficiency. It is preferred for the slip layer (b) to be flexible. If it is not flexible, it could lead to wrinkle formation when subjected to flexing during the transit of the plate, sometimes remaining even after development.

[0023]

It is desired to have adhesion strength between the photosensitive resin layers (a) and slip layer (b) to an extent sufficient to prevent the slip layer

(b) from delaminating during a plate making operation. Sometimes not enough adhesion strength to the resin is obtained if the slip layer (b) has a center line roughness of less than 0.1μm. A plate making treatment by the usual method of the above printing plate components can provide the desired printing plates. The UV light exposure light sources for curing the photosensitive resin used in plate making treatment include high pressure mercury lamps, UV fluorescent lamps, carbon arc lamps, xenon lamps, and the like. Exposure of the photosensitive resin to UV light through a transparent image carrier can provide the objective image.

[0024]

The developer solution for washing out the unexposed areas include chlorinated solvents such as 1,1,1-trifluoroethane, tetrachloroethane, and the like, esters such as heptyl acetate, 3-methoxybutyl acetate, and the like, hydrocarbons such as petroleum fractions, toluene, decalin, and the like, and mixtures of these with alcohols such as propanol, butanol, and the like. The unexposed areas may be washed out by ejection [of the developer] from a nozzle or by brushing. The resultant printing plate is then rinsed, washed, dried and subjected to a post-exposure, thereby generating a printing plate.

[0025]

Hereafter, the invention is explained in detail based on working examples, but the technical scope and embodiments of this invention are not limited to these examples.

[0026]

[Examples 1-4, Comparative Examples 1-3]

The components shown in Table 1 as resin compositions for generation of a photosensitive resin layer (a) were mixed in a kneader thereby generating photosensitive resin compositions. The slip layer (b) was a 100μm thick commercial film for Example 1, and a 20μm thick commercial film for Comparative Example 1; and for others, the layers were prepared from compositions comprised of a polyamide thermoplastic elastomer at the ratios given in Table 2. The compositions were prepared as uniform solutions by adding 30 parts of isopropyl alcohol and 30 parts of toluene to a polyamide (Macromelt 6900, made by Henkel Japan KK) and thermoplastic elastomer (Tuftec M1913, made by Asahi Kasei KK); the resultant composition was applied with a knife coater to a 125μm thick polyester film in such a way that the weight after drying was 4-5g/m^2. This was then dried for 2 minutes at 80°C to generate a slip layer (b) laminated to the polyester film.

[0027]

The center line average roughness of the resultant slip layer (b) at a side

not in contact with the film was measured by a Surcom, a product of Tokyo Seimitsu KK. The resultant slip layer (b) was laminated, via the side thereof having the desired average roughness, onto the photosensitive resin layer (a) and compression-molded with a 1.5mm spacer in a press under the conditions of 130°C for 4 minutes at a pressure of 200kg/cm^2, generating a photosensitive structure for a flexographic printing plate.

[0028]

The resultant photosensitive [structure] for a flexographic printing plate was then exposed at a level of 6000mJ/cm^2 through a transparent image carrier to a UV fluorescent lamp with a center wavelength at 370nm on an AFP-1500 Exposure Apparatus (made by Asahi Kasei KK). The exposure intensity was measured using a Model MO-2 UV Illuminance densitometer, made by ORC Seisaku-sho (Manufacturing Co.,), along with a UV-35 filter, thereby determining the dosage; this was followed by developing on an AFP1500 developer apparatus (made by Asahi Kasei KK) using tetrachloroethylene/n-butanol(3/1 volume ratio), drying for 1 hour at 60°C, and post-exposing for generating a flexographic printing plate. The slip layer which was not needed for the developer was peeled off before the development to be followed thereby.

[0029]

The plate surface roughness R_a of the flexographic printing plate was determined with a VF-7500 instrument, made by Keyence Co.; and the surface tension of the resultant printing plate was measured using a commercial wetness indicator standard solution (made by Wako Junyaku Kogyo KK). Printing quality was monitored by performing a printing test on coated paper using aqueous ink. By noting the ink smudges on the coated paper, an evaluation was made on the basis of the ink coverage of a substrate to be printed. The rating was: ○ for a coverage of 95% or greater; **X** for a level therebelow. As shown in Table 2, Examples 1-4 gave printed products having fine printing quality with good transferability to solid areas at coverages of 95% or higher. On the other hand, Comparative Examples 1-3 gave ink coverages less than 95%, failing to give good printed products or failing to give good adhesion to the photosensitive resin, thereby peeling off before a transparent image carrier was in place, preventing evaluations. These test results are summarized in Table 2.

[0030]

[Table 1]

Photosensitive Resin Composition	% By Weight
Tufprene A (Made by Asahi Kasei KK, a styrene-butadiene-styrene block copolymer)	60
B-2000 (Liquid polybutadiene made by Nippon Sekiyu Kagaku [Petrochemicals] Company)	30
1,9-nonane diol diacrylate	7
2,2-dimethoxy-phenylacetophenone	2
2,6-di-t-butyl-p-cresol	1

[0031]

[Table 2]

	Slip Layer (b)	Slip Layer Surface Roughness Ra (μm)	Printed Plate Surface Tension (dyne/cm)	Printed Plate Surface Roughness Ra (μm)	Transferability to Solid Areas
Example 1	Polyethylene terephthalate film	0.1	39	0.1	○
Example 2	Polyamide 10 parts Thermoplastic elastomer 1 part	0.6	44	0.3	○
Example 3[1)]	Polyamide 10 parts Thermoplastic elastomer 1 part	0.2	46	0.2	○
Example 4[1)]	Polyamide 10 parts Thermoplastic elastomer 2.5 parts	0.2	44	0.2	○
Comp.Ex 1	Chemically treated polypropylene film	9.5	44	0.7	×
Comp.Ex 2	Polyamide 10 parts Thermoplastic elastomer 0 part	0.1	39	0.1	Failed to adhere to the resin, preventing an evaluation
Comp. Ex 3	Polyamide 10 parts Thermoplastic elastomer 40 parts	0.7	44	0.7	×

1) A premixed composition of the polyamide and thermoplastic elastomer with a Labo Plastomill (a product of Toyo Seiki KK) was used.

[0032]

[Advantageous Effect of the Invention

The present invention permits the preparation of a photosensitive resin-based flexographic printing plate that provides a high print quality printed

product with excellent ink transferability in solid areas.

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